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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Alkoxylation of 4-Chloronitrobenzene with Aliphatic Alcohols and Glycols in the Presence of NaOH

E. V. Malykhin and V. D. Shteingarts

Vorozhtsov Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia
e-mail: malykhin@nioch.nsc.ru

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Abstract—The reaction of 4-chloronitrobenzene with aliphatic C_1–*n*–C_4 alcohols and with mono-, di-, and triethylene glycols in the presence of NaOH in liquid ammonia at 15–50°C was studied.

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Alkoxylation of nitrohaloarenes yields alkyl nitrophenyl ethers, which are base intermediates for the synthesis of valuable compounds: dyes [2], pharmaceuticals [3], components for color photography [4], and other materials [5–7]. In alcoholic media, the target process is accompanied by side reactions of nitro group reduction with the formation of aniline derivatives, azobenzenes, and azoxybenzenes [8]. The relative contribution of the transformation pathways largely depends on the volume of the alkyl group in the alcoholate and alcohol and, to a lesser extent, on the mutual location of the halogen atom and nitro group in the aromatic ring, on the ratio and concentrations of the reactants, on the reaction temperature, and on the presence in the reaction mixture of molecular oxygen, water, and agents compensating the nucleophile counterion [9, 10]. For example, to prevent reduction of nitro compounds, methoxy- and ethoxylation of nitrochlorobenzenes is performed in the presence of molecular oxygen [11–14] and of transition metal oxides [15–17] and salts [18, 19], and the oxidation of alkali is suppressed by introducing alkali metal sulfites [20] or urea [21]. With an increase in the volume of the alkyl radical to n-$C_{3,4}$, the nitro group reduction becomes prevalent [9, 10]. Apparently, for this reason, $C_{3,4}$-alkyl ethers of nitrophenols are prepared by the reaction of alkali metal or silver nitrophenolate with the corresponding alkyl halide, mainly with bromide or iodide [22].

Bis-4-nitrophenyl ethers of mono-, di-, and triethylene glycols are used as intermediates in syntheses of the diamine component for polyimides [23–25], rubber antiozonants [26], and drugs [27–31]. It is known that these ethers are formed by fluorine replacement in 4-fluoronitrobenzene under the action of glycols and potassium carbonate in the medium of the nitro compound in ~70% yield [32]. In reactions of 4-chloronitrobenzene with ethylene glycol in the presence of excess KOH and KI in DMF at 140°C [33, 34] or of NaOH and a quaternary ammonium salt in water at 90°C [35], the yield of the corresponding ethylene glycol diether does not exceed 30%. In practice, these diethers, like alkyl nitrophenyl ethers, are prepared by nucleophilic substitution of the halogen atom at the aliphatic carbon atom (of bromine in 1,2-dibromoethane or in 2,2'-dibromodiethyl ether [27, 30, 36–38], of chlorine in 1,2-dichloroethane or 2,2'-dichlorodiethyl ether [39, 40]) under the action of alkali metal 4-nitrophenolate [27, 30, 36–38, 40] or of 4-nitrophenol in the presence of potassium carbonate [39] or of potassium tert-butylate [28] in ethylene glycol [36], diethylene glycol [27, 38], or aprotic bipolar solvents (DMF [39, 40], DMSO [28], dimethylacetamide, *N*-methylpyrrolidone [40]) at 150°C.

It should be emphasized that smooth alkoxydeha-

logenation of nitroarenes under the action of alkali metal alcoholates or of alcohol in the presence of alkali is accomplished by performing fluorine replacement in aqueous/alcoholic media [32] and of other halogens in aprotic bipolar media [39, 40]. However, large-scale use of fluorinated substrates is restricted by their relatively difficult availability, and the use of aprotic bipolar solvents involves problems with the target product isolation and solvent regeneration.

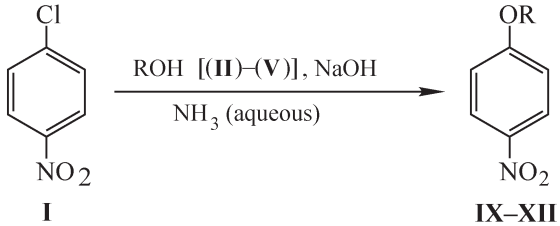
As shown in [41], in liquid ammonia at–33 to –40°C 4-chloronitrobenzene reacts with C_{1-3} alcoholates prepared in situ from the corresponding alcohols and sodium amide to form methyl, ethyl (in 6–10 h), n-propyl, and isopropyl (in 24 h) ethers of 4-nitrophenol with 85–90% conversion of the starting compound. Hence, with liquid ammonia as medium for preparing the alcoholate and performing the reaction, the reagent activity is enhanced owing to minimization of the water content and weak solvation of the anionic nucleophile. However, the most important feature of the process is high selectivity: Practically no products of nitro group reduction are formed. On the whole, high rates of S_NAr reactions involving charged nucleophiles in liquid ammonia, compared to those in aprotic bipolar media [42], and the ease of product isolation and solvent regeneration cause practical interest in processes based on such reactions. In particular, it is appropriate to study in detail the alkoxylation of chloronitroarenes in liquid ammonia. The process would be considerably simplified by eliminating the step of preliminary preparation of the alcoholate by hydrolysis of sodium amide.

In this study we examined the feasibility, efficiency, and selectivity of alkoxydechlorination of 4-chloronitrobenzene (**I**) under the action of aliphatic alcohols [methanol (**II**), ethanol (**III**), *n*-propanol (**IV**), *n*-butanol (**V**)] and glycols [ethylene glycol (**VI**), diethylene glycol (**VII**), triethylene glycol (**VIII**)] in the presence of commercial NaOH in liquid ammonia at temperatures from –33 to 50°C.

The reaction of **I** with alcohol **II** and pulverized NaOH in liquid ammonia at –33°C yield 4-nitroanisole (**IX**) (Scheme 1) in the yield depending on the **I** : **II** : NaOH ratio, which was varied from 1 : 1 : 1 to 1 : 30 : 10 and 1 : 10 : 30 at the process time of 2–25 h. For example, in the reaction of equimolar amounts of the reactants for 5.5 h (Table 1, run no. 1), only 4–6% of I transforms into ether **IX**. With a 3–9-fold amount of NaOH relative to compound **I** and alcohol **II**, taken in the stoichiometric ratio (Table 1, run nos. 2, 3), or with the same excess of alcohol **II** relative to compound **I** and NaOH, taken in the stoichiometric ratio (Table 1, run nos. 4, 5), the conversion of the starting compound increases to 10–17%. When the amounts of both reagents are increased simultaneously (Table 1, run nos. 6–8), the yield increases to 30–50%. If, in addition, the reaction time is made longer (Table 1, run nos. 9–11 and 8, 12, 13), the conversion of **I** can be increased to 65%. To determine the optimal ratio **I** : **II** : NaOH, we analyzed how the conversion of **I** depends on the amounts of NaOH (Table 1, run nos. 4, 6, 10, and 14) and alcohol **II** (Table 1, run nos. 2, 6, 15, and 16–19). The results we obtained show that the optimal ratio ensuring the highest yield of **IX** is **I** : **II** : NaOH = 1 : (2–3) : 1. It is not improbable that this reactant ratio ensures the best balance between the sodium methylate concentration and its activity as nucleophile in the ammonia–alcohol–water system. The product yield does not noticeably change when the reactants are taken in a larger excess relative to the substrate. It should also be noted that compound **I** reacts with alcohol **II** and NaOH at –33°C in liquid ammonia more slowly than with sodium methylate prepared in situ from sodium amide [41], which can be accounted for by the lower activity of the methylate ion in the first case because of its solvation with water.

To attain higher conversion of **I**, the reactions were performed at 10–15°C in a steel autoclave. To demonstrate the process feasibility, we used alkali flakes (see Experimental) without additional pulverization. We found that, at the ratio **I** : **II** : NaOH = 1 : 3 : 1, compound **I** quantitatively transformed into ether **IX** in 5 and 12 h at the substrate : ammonia weight ratio of 1 : 16 (Table 2, run no. 2) and 1 : 1.8 (Table 2, run no. 3). With alcohol **III**, compound **I** reacts more slowly (Table 2,

Scheme 1.



I **IX–XII**

R = CH_3 (**II**, **IX**), C_2H_5 (**III**, **X**), *n*-C_3H_7 (**IV**, **XI**), or *n*-C_4H_9 (**V**, **XII**).

Table 1. Reaction of I (1.57 g) with alcohol II (0.4–4.0 g) and NaOH (0.4–12 g) in liquid ammonia (150 ml) at –33°C

Run no.	**I : II** : NaOH molar ratio	Time τ, h	**I : IX** ratio
1	1 : 1 : 1	5.5	95 : 5
2	1 : 1 : 3	5.5	90 : 10
3	1 : 1 : 9	5.5	89 : 11
4	1 : 3 : 1	5.5	83 : 17
5	1 : 9 : 1	5.5	89 : 11
6	1 : 3 : 3	5.5	67 : 33
7	1 : 5 : 15	5.5	56 : 44
8	1 : 10 : 30	5.5	48 : 52
9	1 : 3 : 9	2.0	94 : 6
10	1 : 3 : 9	5.5	77 : 23
11	1 : 3 : 9	25	35 : 65
12	1 : 10 : 30	2.0	80 : 20
13	1 : 10 : 30	8.0	47 : 53
14	1 : 3 : 27	5.5	83 : 17
15	1 : 4.5 : 3	5.5	64 : 36
16	1 : 6 : 3	5.5	49 : 51
17	1 : 9 : 3	5.5	57 : 47
18	1 : 12 : 3	5.5	55 : 45
19	1 : 27 : 3	5.5	75 : 25

run nos. 1, 2 and 4, 5), but in 17–24 h the transformation into *p*-nitrophenetole is almost quantitative (Table 2, run nos. 6 and 7).

To find conditions for commercial use of the process, we examined the effect of temperature on the result of the reaction of **I** with **II**. We found that, with an increase in temperature to 30 and then to 50°C, higher conversion of **I** is attained already in 5 h (Table 3). However, in this case, in contrast to the reactions at –33 and 10–15°C, we detected products corresponding to the reduction of the nitro group in the starting compound **I** (Table 3, run nos. 1 and 2, 3 and 4), but have not detected anisole derivatives with the nitrogen-containing functional group different from the nitro group. In addition, at the alcohol : alkali ratio close to stoichiometric, the products of the reduction of **I** or of replacement of the halogen atom by the hydroxy group are formed in 3–10 times larger amount than at the 3 : 1 ratio (Table 3, run nos. 1 and 3, 2 and 4). These facts can be accounted for, first, by an increase in the equilibrium concentration of alkali responsible for the formation of 4-nitrophenol and, second, by stronger increase in the rate of side processes with temperature, compared to the rate of formation of the target product. Thus, to minimize the amount of by-products, it is necessary to take the alcohol in excess relative to alkali and to perform the reaction at 10–20°C.

To make the process suitable for technology, it is necessary to provide not only for isolation and purification of the target products to remove NaCl, organic by-products, and excess alcohol, but also for regeneration and reuse of the alcohol and ammonia. Another important item is elimination of the operation of alkali pulverization. We found that these goals can

Table 2. Reaction of **I** with alcohol **II** or **III** and NaOH in liquid ammonia (300–350 ml, 10°C)

Run no.	Reactant amounts, g			**I** : alcohol : NaOH molar ratio	Time τ, h	Product yield, g	Mixture composition, % (GLC data)
	I	alcohol	NaOH				
1	15.7	**II** 4.0	5	1 : 1.2 : 1.2	24	**IX** 14.7–15.0	**IX** >93, (I) 2–5
2	15.7	**II** 9.6	5	1 : 3.0 : 1.2	5	**IX** 14.0–14.4	**IX** >99, (I) 0–0.6
3	100	**II** 62.4	30	1 : 3.0 : 1.2	12	**IX** 103.5	**IX**
4	15.7	**III** 5.6	5	1 : 1.2 : 1.2	24	**X** 14.1	**X** 72.5, (I) 23.2
5	15.7	**III** 13.6	5	1 : 3.0 : 1.2	5	**X** 13.5	**X** 84, (I) 11
6	15.7	**III** 13.6	5	1 : 3.0 : 1.2	17	**X** 14.6	**X** 97.4, (I) 0–2.4
7	100	**III** 88.0	30	1 : 3.0 : 1.2	24	**X** 99.0	**X** 99.4

Table 3. Influence of reaction temperature on the composition of products formed in reaction of I (100 g) with alcohol **II** (31–73 ml) in liquid ammonia (300 ml, **I** : NH_3 = 1 : 18, 2 h)

Run no.	**I** : alcohol : NaOH molar ratio	*T*, °C	Product yield, % (GLC data)					
			IX	**I**	4-nitrophenol	4,4'-dichloro-azoxybenzene	4,4'-dichloro-azobenzene	4-chloroaniline
1	1 : 1.2 : 1.2	28	79–81	8–12	0.5–0.6	5–6	0.3–0.4	1.5–3
2	1 : 1.2 : 1.2	50	84–86	0.5–1.5	2.0–2.5	7–8.5	1.0–1.2	2–3
3	1 : 3 : 1.2	28	90–94	4.5–8.5	0.5–0.6	1.3–1.7	–	<0.2
4	1 : 3 : 1.2	50	94–95	1–2	0.7–1.0	3.4–3.8	–	<0.2

be accomplished by successively performing the following operations: (a) condensation of the major fraction of ammonia distilled off from the reaction mixture; (b) heating of the remaining mixture of the products with water; (c) distillation of aqueous alcohol from the aqueous-organic mixture, followed by the alcohol recovery by rectification; (d) separation of the hot aqueous-organic residue after distillation of aqueous alcohol to the organic and aqueous layers. In Table 4, we give the quality characteristics and yields for ethers **IX** and **X** obtained using the above procedures with commercial alkali flakes (run nos. 1, 3), and also for the regenerated alcohol and ammonia (run nos. 2, 4). It should be emphasized that these data refer to crude products, not subjected to additional purification. Using the optimal ratio alcohol : alkali = 3 : 1 and the developed procedure, we prepared 4-nitro-*n*-propoxy- and -*n*-butoxybenzenes (**XI** and **XII**, respectively) in high yields (Table 4, run nos. 5, 6).

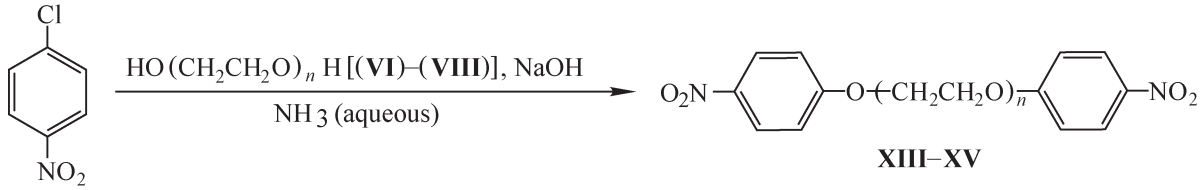
Acceptable time of the synthesis of alkyl nitrophenyl ethers and high quality of the products gave grounds to examine the synthesis of bis-*p*-nitrophenyl ethers of glycols by the similar procedure (Scheme 2).

Data on the yields of mono-, di-, and triethylene glycol bis-4-nitrophenyl ethers **XII**–**XIV** formed by reactions of compound **I** with glycols **VI–VIII**, respectively, and the process conditions are given in Table 5.

We found that the starting compound **I** is practically fully consumed within 10–15 h at *T* ~50°C. The content of the initially formed glycol mononitrophenyl ethers in the reaction products is low, and that of the target products **XII–XIV** is high, suggesting higher nucleophilic activity of salts of glycol mononitrophenyl ethers, compared to the salts of the starting glycols. At the same time, 4-nitrophenol is formed in higher yield relative to the desired diethers (up to ~10% in the reaction with glycol **VIII**) than in the reaction with alcohols. The results can probably be accounted for by ratios of the equilibrium concentrations of alkali, glycol alcoholates, and glycol monoether alcoholates and of the solubilities of their salts and neutral compounds present in the reaction mixture [43].

Thus, liquid ammonia at moderate temperatures (15–50°C) is highly efficient as solvent for alkoxydechlorination of 4-chloronitrobenzene by the action of aliphatic alcohols and glycols in the presence of NaOH. The use of this solvent allows the yield of compounds with the reduced nitro group (chlorinated amino, azo, azoxy compounds), significant in the reactions performed in alcohols, to be minimized. The mono- and bis-4-nitrophenyl ethers obtained are high-quality products suitable for further use without additional purification. These chemical and technological advantages

Scheme 2.



I **XIII**–**XV**

n = 1 (**VI**), (**XIII**); 2 (**VII**), (**XIV**); 3 (**VIII**), (**XV**).

Table 4. Reaction of **I** with alcohols **II–V** and NaOH flakes at 10–20°C

Run no.	Reactant amounts, g				τ, h	Product yield, g (%)	Purity, % (GLC data)
	I	alcohol	NaOH	NH_3(g)			
1	70.0	**II** 45.0	21.0	123	12	**IX** 65.0 (95.6)	99.8
2	70.0	**II** 22+23[a]	21.0	31+92[b]	12	**IX** 66.3 (97.5)	99.8
3	52.5	**III** 46.9	15.8	102	15	**X** 54.2 (97.4)	99.3
4	52.5	**III** 24.5+22.4[a]	15.8	25+77[b]	15	**X** 53.8 (96.6)	99.4
5	35.0	**IV** 40.0	10.5	70	10	**IX** 39.5 (98.2)	96.8
6	52.5	**V** 73.6	15.7	110	10	**XII** 54.8 (84.3)	99

[a] Regenerated alcohol.

[b] Regenerated ammonia.

Table 5. Reaction of **I** (12.6 g) with diols **VI–VIII** and NaOH in liquid ammonia (150 ml)

Run no.	Reactant amounts, g		τ, h	*T*, °C	Product yield, g (%)				
	diol	NaOH			diether	monoether	4-nitro-aniline	4-nitro-phenol	**I**
1	**VI** 2.48	8.0	15	15	**XIII** 77.4 (9.4)	1.4 (0.4)	0.6 (0.2)	0.6 (0.2)	18.2 (2.5)
2	**VI** 2.48	4.0	15	50	**XIII** 88.0 (10.7)	4.0	0.4	2.8	–
3	**VII** 4.24	4.0	10	15	**XIV** 85.7 (11.9)	1.3	–	3.6	6.4
4	**VII** 4.24	4.0	10	65	**XIV** 87.5 (12.1)	1.1	0.6	2.3	1.1
5	**VIII** 6.0	4.0	15	15	**XV** 90.0 (12.5)	0.7	–	10	–

of the process performed in liquid ammonia as solvent make this process promising for commercial synthesis of alkyl nitrophenyl ethers by alkoxydechlorination of chloronitroarenes. This process can become an alternative to processes based on the same reactions performed in alcohols or on nucleophilic substitution of the halogen atom at the carbon atom under the action of nitrophenolate ions.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded with a Bruker AC-200 device using as internal reference the signal of residual protons in acetone-d_6. The IR spectra were measured with a Bruker Vector-22 device using samples pelletized with calcined KBr. The GLC–MS identification of the components was performed with an HP G1081A complex consisting of an HP 5890 Series II chromatograph and an HP 5971 mass-selective detector. The ionizing electron energy was 70 eV. We used a column 30 m long, 0.25 mm i.d., coated with a 0.25-μm layer of HP 5 stationary phase (5% diphenyl-/95% dimethylsiloxane). The carrier gas was He, flow rate 1 ml min^{-1}. The column was kept for 2 min at 50°C, then heated at a rate of 10 deg min^{-1} to 280°C, and kept at the final temperature for 5 min. The vaporizer temperature was 280°C, and the ion source temperature, 173°C. The mass spectra were scanned in the range 30–550 amu at a rate of 1.2 scan s^{-1}. The mixture compositions were determined by GLC (internal normalization) with an HP 5890 device (thermal conductivity detector). In these experiments, we used a quartz capillary column 30 m long, 0.22 mm i.d., coated with HP 5 stationary phase (layer thickness 2.6 μm). The carrier gas was He, flow rate 1 ml min^{-1}. The column was kept for 2 min at 90°C, then heated at a rate of 10 deg min^{-1} to 330°C, and finally kept at 330°C. The vaporizer and detector temperatures were 300 and 320°C, respectively. The melting points of samples were determined with a Temp-2 device in the automatic mode.

We used commercial chemicals without pretreatment:

technical-grade liquid ammonia (grade A, supreme, or I); 4-nitrochlorobenzene, grade II; methanol; ethanol; pure grade ethylene glycol, *n*-propanol, *n*-butanol, diethylene glycol, and triethylene glycol; technical-grade sodium hydroxide (TR OKP 213211 grade) was pulverized in a porcelain mortar in a dry box or used without pretreatment (TKh brand, grade I, flakes); potable water; gaseous nitrogen; pharmacopoeial grade diethyl ether; chemically pure grade benzene; concentrated sulfuric acid; ammonium chloride. Methyl *tert*-butyl ether was purified by fractional distillation (99%, GLC, internal normalization); pure grade magnesium sulfate was calcined at 400°C and stored in a sealed vessel.

Alkoxylation of **I** with alcohol **II** or **III** and NaOH in an open vessel at –33°C (general procedure). An elongated round-bottomed glass flask placed in a Dewar vessel for temperature control and equipped with a power-driven stirrer, a thermometer, and a gas removal tube was charged in a stream of dry nitrogen gas with pulverized NaOH and with 200 ml of liquid ammonia. After that, we added with stirring the alcohol (dropwise) and then compound **I** (in small portions). The mixture was stirred for the required time, with monitoring the level of ammonia in the flask and adding ammonia, when necessary, to maintain the initial volume. After the end of the reaction period, ammonium chloride was added in a 3–5-fold amount relative to the alkali, the cooling was ceased, and the ammonia was allowed to evaporate. The residue was processed as described below.

Alkoxylation of I with aliphatic alcohols or glycols in the presence of NaOH in an autoclave at 15–50°C (general procedure). A 200–500-ml stainless steel autoclave (Vishnevskii's vessel) equipped with a blade stirrer was charged with 4-nitrochlorobenzene, alcohol or glycol, and NaOH flakes. The vessel was sealed, stirring was switched on, and 100–175 ml of ammonia was introduced into the autoclave from a thick-walled volumetric glass vessel equipped with a counterpressure unit. The mixture was stirred for 5–15 h at 15 or 50–65°C. The ammonia was distilled off from the reaction mixture into a Dewar vessel cooled to –50°C.

In the synthesis of alkyl 4-nitrophenyl ethers, 110 g of water was added to the residue in the autoclave, the autoclave was sealed, and a mixture of alcohol and water was distilled off at vapor temperatures of up to 98°C. The hot (70–80°C) bottom residue was filtered off on a heated pressure filter through a layer of coarse calico on belting. 4-Nitrophenyl ether was isolated from the filtrate after its phase separation in a heated separating funnel.

To identify the by-products and determine their amount, we performed extraction from the aqueous layer with methyl tert-butyl or diethyl ether (3 × 30 ml). The combined extracts were dried over calcined magnesium sulfate, filtered, and evaporated. Chlorinated aromatic compounds, 4-nitroaniline, and unchanged 4-chloronitrobenzene were quantitatively determined in the dry residue by GLC (calibration using artificially prepared mixtures). The aqueous solution was cooled to 0°C and acidified with 10% sulfuric acid to pH ~2–3, after which the solid product containing 4-nitrophenol was isolated by extraction with diethyl ether (3 × 30 ml).

By this general procedure [44], we prepared 4-nitroanisole (**IX**, mp 49–53°C; published data: mp 54°C [45]), 4-nitrophenetole (**X**, mp 53–56°C; published data: mp 60°C [45]), 4-nitro-n-propoxybenzene (**XI**, bp 163–165°C/20 mm Hg; published data: bp 285–287°C [46], 135–137°C/8 mm Hg [41]), and 4-nitro-*n*-butoxybenzene (**XII**, mp 30–33°C; published data: mp 32–33°C [47].

The ^{1}H NMR and IR spectra of ethers **IX–XI** are identical to those given in [48].

In preparation of glycol bis-4-nitrophenyl ethers, the reaction mixture was transferred onto a porous glass filter, with thoroughly washing off the mixture from autoclave walls with hot water (3 × 30 ml), washed on the filter with hot water (5 × 20 ml), squeezed, and dried in air to constant weight. The solid mass was washed on the filter in succession with benzene (2 × 20 ml) and diethyl ether (2 × 20 ml) and dried to constant weight to obtain diethers **XIII–XV**.

For exhaustive determination of the reaction products, we performed extraction of wash waters. For this purpose, we combined the ether and benzene extracts obtained when washing the desired solid product and extracted wash waters with them. The extract was dried over calcined magnesium sulfate, the solvents were evaporated, and the solid residue was analyzed as described above for alkyl 4-nitrophenyl ethers. Then the wash waters were cooled to 0°C, acidified with 10% sulfuric acid to pH ~2–3, and extracted with diethyl ether (3 × 30 ml). The extract was dried over calcined magnesium sulfate and evaporated to dryness to obtain a mixture of 4-nitrophenol and glycol 4-nitrophenyl ether, which were identified and quantitatively determined by gas chromatography–mass spectrometry.

By this general procedure, we prepared 1,2-bis(4-nitrophenoxy)ethane (**XIII**, mp 149.5–150°C; published data: mp 147°C [37], 148–149°C [27–31]), bis-2-(4-nitrophe-

noxy)ethyl ether {**XIV**, mp 156.8–158.0°C (from ethanol); published data: mp 155–156°C [27–31], 154–157°C [38]}, and 1,2-bis[2-(4-nitrophenoxy)ethoxy]ethane (**XV**, mp 95–98°C; published data: mp 96–97°C [27–31]). Found, %: C 55.05, H 5.03, N 7.02. $C_{18}H_{20}N_2O_8$. Calculated, %: C 55.10, H 5.09, N 7.10. ^{1}H NMR spectrum (δ, ppm): 3.9 m (12H, $–OCH_2CH_2O–$), 7.6 q (8H, $C_{ar}–H$). IR spectrum (ν, cm^{-1}): 1350 and 1530 (NO_2).

CONCLUSIONS

(1) The chlorine atom in 4-nitrochlorobenzene is efficiently replaced under the combined action of alkyl alcohols ($C_{1–4}$) or diols (mono-, di-, triethylene glycols) and NaOH in liquid ammonia at relatively low temperatures (15–50°C) to form the corresponding alkyl 4-nitrophenyl mono- and diethers of high quality in high yields.

(2) In contrast to the processes in alcoholic media, alkoxydechlorination of 4-nitrochlorobenzene in liquid ammonia at temperatures below 30°C is not accompanied by side reactions of the nitro group reduction in the starting compound and products.

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